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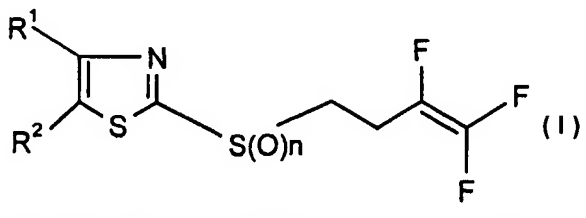
(54) Title: NEMATICIDAL TRIFLUOROBUTENE DERIVATIVES



(I)

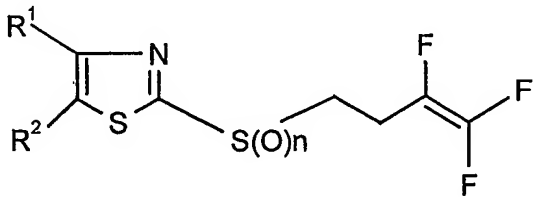
(57) Abstract: The present invention relates to novel trifluorobutene derivatives of the following formula (I) wherein R1 represents hydrogen, halogen, alkyl, haloalkyl, cycloalkyl or alkoxycarbonylmethyl,R2 represents hydrogen, halogen, alkyl, alkoxyalkyl, alkylthioalkyl, carboxy, alkylaminocarbonyl, cycloalkylaminocarbonyl, dialkylaminocarbonyl or alkoxycarbonyl, and n represents 0, 1 or 2,with the proviso that R1 and R2 do not represent hydrogen at the same time, and in case R1 represents hydrogen, then R2 does not represent halogen, to a process for their preparation and to their use as nematicides.

NEMATICIDAL TRIFLUOROBUTENE DERIVATIVES

The present invention relates to novel trifluorobutene derivatives, to processes for their preparation and to their use as nematicides.

U. S. Patent No. 3,513,172 describes trifluorobutenyl compounds with nematicidal activity. Japanese Laid-open Patent Publication (PCT) No. 500037/1988 also refers to polyhaloalkene compounds with nematicidal activity. Further, WO95/24403 describes that 4,4-difluorobutenyl compounds have nematicidal activity.

There have now been found novel trifluorobutene derivatives of the following formula (I)



(I),

wherein

R^1 represents hydrogen, halogen, alkyl, haloalkyl, cycloalkyl or alkoxycarbonylmethyl,

R^2 represents hydrogen, halogen, alkyl, alkoxyalkyl, alkylthioalkyl, carboxy, alkylaminocarbonyl, cycloalkylaminocarbonyl, dialkylaminocarbonyl or alkoxycarbonyl, and

n represents 0, 1 or 2,

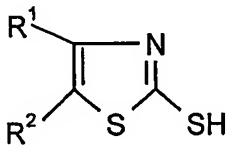
with the proviso that R^1 and R^2 do not represent hydrogen at the same time, and in case R^1 represents hydrogen, then R^2 does not represent halogen.

The compounds of the above-mentioned formula (I) can be synthesized, for example, by the following preparation processes a), b) or c).

Preparation process a)

To obtain compounds of the formula (I) wherein n represents 0,

compounds of the formula (II)

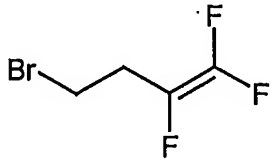


(II)

wherein

R^1 and R^2 have the aforementioned definitions,

are reacted with 4-bromo-1,1,2-trifluoro-1-butene

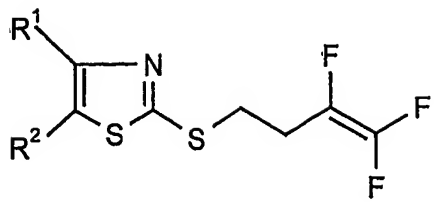


in the presence of inert solvents and, if appropriate, in the presence of an acid binder.

Preparation process b)

To obtain compounds of the formula (I) wherein n represents 1 or 2,

compounds of the formula (Ia)



(Ia)

wherein

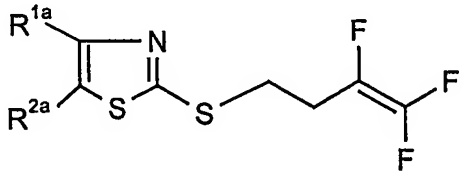
R^1 and R^2 have the aforementioned definitions,

are oxidized in the presence of inert solvents.

Preparation process c)

To obtain compounds of the formula (I) wherein R^1 represents haloalkyl, R^2 represents hydrogen and n represents 0,

compounds of the formula (Ib)



(Ib)

wherein

R^{1a} represents alkyl, and

R^{2a} represents hydrogen,

are reacted with a halogenating agent in the presence of inert solvents.

The compounds of the formula (I) of the present invention show strong nematicidal activity and good compatibility with various crops.

According to the present invention, the compounds of the formula (I) provide for an unexpectedly high nematicidal activity compared with the compounds described in the aforementioned prior art.

In the specification, "halogen" represents fluoro, chloro, bromo or iodo, preferably represents fluoro, chloro or bromo, and particularly preferably represents chloro or bromo.

In the specification, hydocarbon chains, such as "alkyl" –also in connection with other moieties, such as "alkoxycarbonylmethyl", "alkoxyalkyl", "alkylthioalkyl", "alkylaminocarbonyl", "dialkylaminocarbonyl" or "alkoxycarbonyl"- are in each case straight-chain or branched-chain, such as methyl, ethyl, n- or iso-propyl, n-, iso-, sec- or tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl etc.

In the specification "alkyl" preferably represents C_{1-8}-alkyl, more preferably represents C_{1-6}-alkyl, and particularly preferably represents C_{1-4}-alkyl.

In the specification "haloalkyl" represents "alkyl" substituted with at least one "halogen", preferably represents C_{1-4}-alkyl substituted with one or a plurality of halogen, and particularly preferably represents C_{1-3}-alkyl substituted with one or a plurality of fluoro, chloro and/or bromo. Examples for such "haloalkyl" moieties are for example chloromethyl, bromomethyl, trifluoromethyl.

In the specification "cycloalkyl" –also in connection with other moieties, such as "cycloalkylaminocarbonyl"- represents e.g. cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl etc. "Cycloalkyl" preferably represents C_{3-6}-cycloalkyl, and particularly preferably represents cyclopropyl, cyclopentyl or cyclohexyl.

In as far as the compounds of the formula (I) according to the present invention contain substituents with asymmetric carbon atoms, the invention relates in each case to the R enantiomers and the S enantiomers and to any mixtures of these enantiomers, in particular to the racemates.

Preferred meanings of the above defined substituents of the compounds of the formula (I) are given below.

R^1 preferably represents hydrogen, fluoro, chloro, bromo, C_{1-6}-alkyl or C_{1-3}-haloalkyl, C_{3-6}-cycloalkyl or C_{1-4}-alkoxycarbonylmethyl.

R^2 preferably represents hydrogen, fluoro, chloro, bromo, carboxy, C_{1-6}-alkyl, C_{1-4}-alkoxy-C_{1-4}-alkyl, C_{1-4}-alkylthio-C_{1-4}-alkyl, C_{1-4}-alkylaminocarbonyl, C_{3-6} cycloalkylaminocarbonyl, di-C_{1-4}-alkylaminocarbonyl or C_{1-4}-alkoxycarbonyl.

n preferably represents 0 or 2.

R^1 particularly preferably represents hydrogen, fluoro, chloro, bromo, methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, chloromethyl, bromomethyl, trifluoromethyl, cyclopropyl, cyclopentyl, cyclohexyl, methoxycarbonylmethyl, ethoxycarbonylmethyl or n-propoxycarbonylmethyl.

R^2 particularly preferably represents hydrogen, chloro, methyl, ethyl, methoxymethyl, ethoxymethyl, methylthiomethyl, ethylthiomethyl, carboxy, methylaminocarbonyl, ethylaminocarbonyl, n-propylaminocarbonyl, isopropylaminocarbonyl, n-butylaminocarbonyl, sec-butylaminocarbonyl, cyclopropylaminocarbonyl, cyclopentylaminocarbonyl, cyclohexylaminocarbonyl, dimethylaminocarbonyl, diethylaminocarbonyl, methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl or isopropoxycarbonyl.

n particularly preferably represents 0.

A very especially preferred group are the compounds of the formula (I), wherein

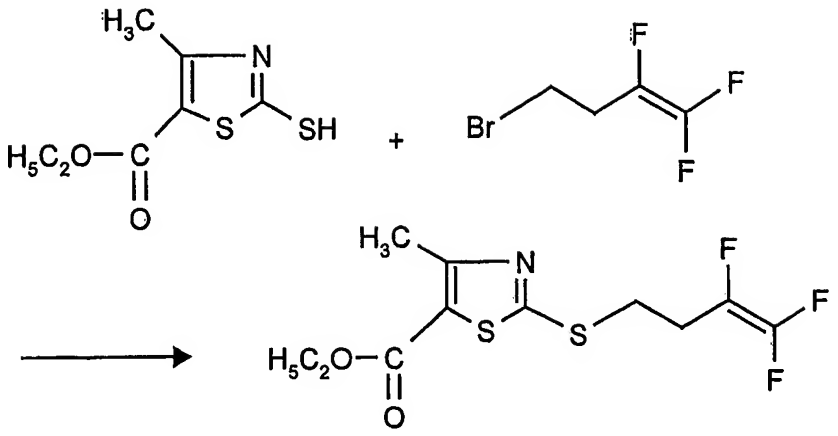
R^1 represents hydrogen, fluoro, chloro, bromo, methyl, ethyl, n- or i-propyl or n-, i-, s-, or t-butyl, chloromethyl, bromomethyl, trifluoromethyl, cyclopropyl, cyclopentyl, cyclohexyl, methoxycarbonylmethyl, ethoxycarbonylmethyl, n- or i-propoxycarbonylmethyl,

R^2 represents hydrogen, fluoro, chloro, methyl, ethyl, n- or i-propyl, n-, i-, s-, or t-butyl, methoxymethyl, ethoxymethyl, methylthiomethyl, ethylthiomethyl, carboxy, methylaminocarbonyl, ethylaminocarbonyl, n- or i-propylaminocarbonyl, n-, i-, s-, or t-butylaminocarbonyl, cyclopropylaminocarbonyl, cyclopentylaminocarbonyl, cyclohexylaminocarbonyl, dimethylaminocarbonyl, diethylaminocarbonyl, methoxycarbonyl, ethoxycarbonyl or n- or i-propoxycarbonyl, and

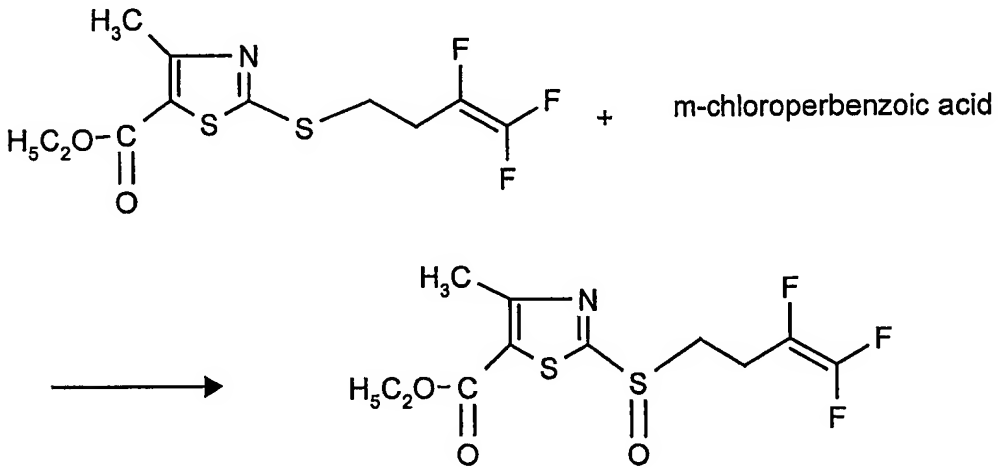
n represents 0, 1 or 2,

with the proviso that $R^1$and R^2 do not represent hydrogen at the same time, and in case R^1 represents hydrogen, then R^2 does not represent chloro.

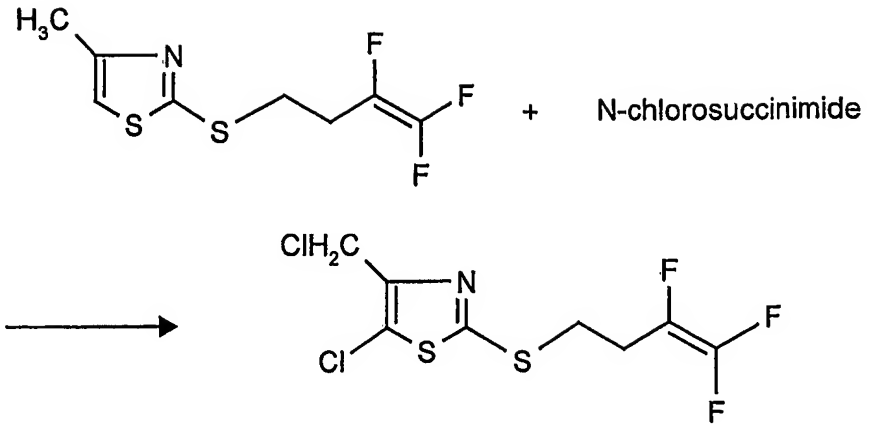
The aforementioned preparation process a) for preparing a compound of the formula (I) of the present invention can be represented by the following reaction scheme when, for example, 5-ethoxycarbonyl-2-mercapto-4-methylthiazole and 4-bromo-1,1,2-trifluoro-1-butene are used as starting material.



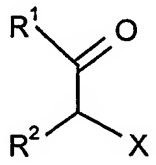
The preparation process b) for preparing a compound of the formula (I) of the present invention can be represented by the following reaction scheme when, for example, 5-ethoxycarbonyl-4-methyl-2-(3',4',4'-trifluoro-3'-butenylthio)thiazole is used as starting material and m-chloroperbenzoic acid is used as oxidizing agent.



Finally, the preparation process c) for preparing a compound of the formula (I) of the present invention can be represented by the following reaction scheme when, for example, 4-methyl-2-(3',4',4'-trifluoro-3'-butenylthio)thiazole is used as starting material and, for example, N-chlorosuccinimide is used as halogenating agent.



The compounds of the formula (II) which are being used as starting material in the aforementioned preparation process a), partly include known compounds. They can generally be obtained by reacting a ketone represented by the formula (III)



(III)

wherein

R^1 and R^2 have the aforementioned definition, and

X represents halogen,

with ammonium dithiocarbamate.

The above-mentioned reaction is known per se. The reaction is described, for example, in *Bull. Soc. Chem. Fr.*, 1948 (1967) and *Bull. Soc. Chem. Fr.*, 2863 (1968).

The ketones of the formula (III) used in the above-mentioned reaction can be prepared, for example, according to the process described in SHIN-JIKKEN

KAGAKU KOUZA (New Lecture of Experimental Chemistry) 14 (1), 346-351, (1977) (published by MARUZEN).

The following examples of compounds of the formula (II) can be prepared according to the above described process:

2-mercapto-4-trifluoromethylthiazole, 2-mercapto-4-methylthiazole, 4-ethyl-2-mercaptothiazole, 4-cyclopropyl-2-mercaptothiazole, 5-diethylaminocarbonyl-2-mercaptothiazole, 5-isopropylaminocarbonyl-2-mercaptothiazole, 2-mercapto-5-methoxymethylthiazole, 2-mercapto-5-methylaminocarbonylthiazole, 5-cyclopropylaminocarbonyl-2-mercaptothiazole, 5-dimethylaminocarbonyl-2-mercaptothiazole, 5-diethylaminocarbonyl-2-mercaptothiazole, 2-mercapto-5-methylthiomethylthiazole, 2-mercapto-5-methoxycarbonyl-4-methylthiazole etc.

4-Bromo-1,1,2-trifluoro-1-butene, used as starting material in the aforementioned preparation process a), is a known compound which was described, for example, in WO 86/07590.

The compounds of the formula (Ia), used as starting material in the aforementioned preparation process b), correspond to the compounds of formula (I), wherein n represents 0. They can be synthesized, for example, according to the aforementioned preparation process a).

The oxidizing agents used for oxidation of a compound of the above-mentioned formula (Ia) in the preparation process b) are widely used in the field of organic chemistry. Such compounds are, for example, hydrogen peroxide water, m-chloroperbenzoic acid, peracetic acid, perbenzoic acid, magnesium monoperoxyphthalate, potassiumperoxymonosulfate etc.

The compounds of the formula (Ib), used as starting material in the aforementioned preparation process c), are described by the compounds of the formula (I) wherein n

represents 0. They can be synthesized, for example, according to the aforementioned preparation process a).

The halogenating agents, which are reacted with the compounds of the formula (Ib) in the preparation process c) are widely used in the field of organic chemistry. Such compound include, for example, sulfuryl chloride, N-chlorosuccinimide, N-bromo-succinimide, trichloroisocyanuric acid, potassium fluoride, chlorine gas, bromine, iodine etc.

The reaction of the preparation process a) can be conducted in the presence of an adequate diluent. The following diluents can, for example, be used in the process: aliphatic, alicyclic and aromatic hydrocarbons, for example, hexane, cyclohexane, petroleum ether, ligroine, benzene, toluene, xylene etc.; ethers, for example, diethyl ether, methyl ethyl ether, di-isopropyl ether, dibutyl ether, propylene oxide, dioxane, tetrahydrofuran etc.; ketones, for example, acetone, methyl ethyl ketone, methyl isobutyl ketone etc.; nitriles, for example, acetonitrile, propionitrile, acrylonitrile etc.; acid amides, for example, dimethylformamide, dimethylacetamide, N-methyl-pyrrolidone etc.

The reaction of the preparation process (a) can be conducted in the presence of an acid binder. The following acid binders can, for example, be used in the process: hydroxides, carbonates and alcoholates etc. of alkali metals, tertiary amines, for example, triethylamine, diethylaniline, pyridine, 4-dimethylaminopyridine, ,4-diazabicyclo[2,2,2]octane (DABCO), 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) etc.

The reaction of the preparation process a) can be conducted in a substantially wide range of temperature. However, the temperatures in a range of generally about 0°C to about 150°C, preferably about 20°C to about 100°C are especially suitable.

Although said reaction is desirably conducted under normal pressure, it can be optionally conducted under elevated pressure or under reduced pressure.

In conducting the preparation process a), the compound of the corresponding formula (I) can be obtained, for example, by reacting 0.7-1.5 moles of 4-bromo-1,1,2-trifluoro-1-butene with 1 mole of the compound of the formula (II) in a diluent, for example, acetonitrile in the presence of 1-1.3 moles of a condensing agent, for example, potassium carbonate, under reflux by heating.

Among the compounds of the formula (I) of the present invention which can be prepared by the preparation process a), the compounds wherein R^1 represents hydrogen and R^2 represents carboxy, alkylaminocarbonyl or alkoxyalkyl, as well as the compounds wherein R^1 and R^2 each represent halogen, can equally be synthesized by other processes as described in the below synthesis examples (4-7).

The reaction of the preparation process b) can be conducted in the presence of an adequate diluent. The following diluents can, for example, be used in the process: aliphatic, alicyclic and aromatic hydrocarbons (which may be optionally chlorinated), for example, hexane, cyclohexane, petroleum ether, ligroine, benzene, toluene, xylene, methylene chloride, chloroform, carbon tetrachloride, ethylene chloride, chlorobenzene etc.; ethers, for example, diethyl ether, methyl ethyl ether, di-isopropyl ether, dibutyl ether, dioxane, tetrahydrofuran etc.; alcohols, for example, methanol, ethanol, isopropanol, butanol, ethylene glycol etc.; esters, for example, ethyl acetate, amyl acetate etc.; acid amides, for example, dimethylformamide, dimethylacetamide, N-methylpyrrolidone etc.; carboxylic acids, for example, formic acid, acetic acid etc.

The reaction of the preparation process b) can be conducted in a substantially wide range of temperature. However, the temperatures in a range of generally about -20°C to about 100°C, preferably about 0°C to about 80°C are especially suitable.

Although said reaction is desirably conducted under normal pressure, it can also be conducted under elevated pressure or under reduced pressure.

In conducting the preparation process b), the compound of the corresponding formula (I) can be obtained, for example, by reacting, for example, 0.8-3 moles of m-chloroperbenzoic acid with 1 mole of the compound of the formula (Ia) in a diluent, for example, methylene chloride, at room temperature.

The reaction of the preparation process c) can be conducted in the presence of an adequate diluent. The following diluents can, for example, be used in the process: aliphatic, alicyclic and aromatic hydrocarbons (which may be optionally chlorinated), for example, hexane, cyclohexane, petroleum ether, ligroine, benzene, toluene, xylene, methylene chloride, chloroform, carbon tetrachloride, ethylene chloride, chlorobenzene etc.; ethers, for example, diethyl ether, methyl ethyl ether, di-isopropyl ether, dibutyl ether, dioxane, tetrahydrofuran etc.; acid amides, for example, dimethylformamide, dimethylacetamide, N-methylpyrrolidone etc.; sulfones and sulfoxides, for example, dimethyl sulfoxide, sulfolane etc.

The reaction of the preparation process c) can be conducted in a substantially wide range of temperature. However, the temperatures in a range of generally about -20°C to about 200°C, preferably about 0°C to about 150°C are especially suitable.

Although said reaction is desirably conducted under normal pressure, it can be optionally conducted under elevated pressure or under reduced pressure.

In conducting the preparation process c), the compound of the corresponding formula (I) can be obtained, for example, by reacting 1-4 moles of N-chlorosuccinimide with 1 mole of the compound of the formula (Ib) in a diluent, for example, carbon tetrachloride, under reflux by heating.

The compounds of the formula (I) of the present invention display a strong controlling activity against nematodes. They can, therefore, be efficiently used as nematicidal agents, for example, in the field of agriculture and forestry. It is important to note that the compounds of the formula (I) of the present invention do

not show phytotoxicity against crops while at the same time effectively controlling harmful nematodes.

The compounds according to the invention can be used, for example, against nematodes such as Pratylenchus spp., Globodera spp., such as Globodera rostochiensis wollenweber, Heterodera spp., such as Heterodera glycines ichinohe, Meloidogyne spp., Aphelenchoides spp., such as Aphelenchoides basseyi christie, Radopholus similis, Ditylenchus dipsaci, Tylenchulus semipenetrans, Longidorus spp., Xiphinema spp., Trichodorus spp., Bursaphelenchus spp., such as Bursaphelenchus xylophilis etc.

The compounds according to the invention are especially useful for combating Pratylenchus spp., Globodera rostochiensis wollenweber, Heterodera glycines ichinohe, Meloidogyne spp., Aphelenchoides basseyi christie, Bursaphelenchus xylophilis.

However, the use of the active compounds according to the invention is in no way restricted to these genera, but also extends in the same manner to other nematodes.

The active compounds of the present invention can exist also as a mixed agent with other active compounds, for example, insecticides, bactericides, miticides, fungicides etc. in the form of their commercially useful formulation or in the application form prepared from those formulations. Here, as insecticides, there can be mentioned, for example, organophosphorous agents, carbamate agents, carboxylate type chemicals, chlorinated hydrocarbon type chemicals, chloronicotinyl type chemicals, insecticidal substances produced by microbes etc.

The active compounds according to the invention, as such or in their formulations, can also be used in a mixture with known fungicides, bactericides, acaricides, nematicides or insecticides, to widen, for example, the activity spectrum or to prevent the development of resistance. In many cases, this results in synergistic effects, i.e.

the activity of the mixture exceeds the activity of the individual components. Such formulations and application forms are commercially and ecologically especially useful as generally lower amounts of active ingredients can be used. A synergist, however, must not necessarily be active itself, as long as it enhances the action of the active compound.

The content of the active compounds of the present invention in a commercially useful formulation or application form can be varied in a wide range. The active-compound content of the use forms prepared from the commercial formulations can vary within wide limits. The active-compound concentration of the use forms can be from 0.0000001 to 100 % by weight of active compound, preferably between 0.0001 and 1 % by weight.

Examples of particularly advantageous mixing components are the following:

Fungicides

aldimorph, ampropylfos, ampropylfos potassium, andoprim, anilazine, azaconazole, azoxystrobin, benalaxyl, benodanil, benomyl, benzamacril, benzamacril-isobutyl, bialaphos, binapacryl, biphenyl, bitertanol, blasticidin-S, bromuconazole, bupirimate, buthiobate, calcium polysulphide, capsimycin, captafol, captan, carbendazim, carboxin, carvon, quinomethionate, chlobenthiazone, chlorfenazole, chloroneb, chloropicrin, chlorothalonil, chlozolinate, clozylacon, cufraneb, cymoxanil, cyproconazole, cyprodinil, cyprofuram, debacarb, dichlorophen, diclobutrazole, diclofluanid, diclomezine, dicloran, diethofencarb, difenoconazole, dimethirimol, dimethomorph, diniconazole, diniconazole-M, dinocap, diphenylamine, dipyrithione, ditalimfos, dithianon, dodemorph, dodine, drazoxolon, ediphenphos, epoxiconazole, etaconazole, ethirimol, etridiazole, famoxadon, fenapanil, fenarimol, fenbuconazole, fenfuram, fenitropan, fenpiclonil, fenpropidin, fenpropimorph, fentin acetate, fentin hydroxide, ferbam, ferimzone, fluazinam, flumetover, fluoromide, fluquinconazole, flurprimidol, flusilazole, flusulfamide, flutolanil, flutriafol, folpet, fosetyl-

aluminium, fosetyl-sodium, fthalide, fuberidazole, furalaxyl, furametpyr, furcarbonil, furconazole, furconazole-cis, furmecyclox, guazatine, hexachlorobenzene, hexaconazole, hymexazole, imazalil, imibenconazole, iminoctadine, iminoctadine albesilate, iminoctadine triacetate, iodocarb, ipconazole, iprobenfos (IBP), iprodione, irumamycin, isoprothiolane, isovaledione, kasugamycin, kresoxim-methyl, copper preparations, such as: copper hydroxide, copper naphthenate, copper oxychloride, copper sulphate, copper oxide, oxine-copper and Bordeaux mixture, mancopper, mancozeb, maneb, meferimzone, mepanipyrim, mepronil, metalaxyl, metconazole, methasulfocarb, methfuroxam, metiram, metomeclam, metsulfovax, mildiomycin, myclobutanil, myclozolin, nickel dimethyldithiocarbamate, nitrothal-isopropyl, nuarimol, ofurace, oxadixyl, oxamocarb, oxolinic acid, oxycarboxim, oxyfenthiin, paclobutrazole, pefurazoate, penconazole, pencycuron, phosdiphen, pimaricin, piperalin, polyoxin, polyoxorim, probenazole, prochloraz, procymidone, propamocarb, propanosine-sodium, propiconazole, propineb, pyrazophos, pyrifenox, pyrimethanil, pyroquilon, pyroxyfur, quinconazole, quintozene (PCNB), sulphur and sulphur preparations, tebuconazole, tecloftalam, tecnazene, tetcyclacis, tetraconazole, thiabendazole, thicyofen, thifluzamide, thiophanate-methyl, thiram, tioxymid, tolclofos-methyl, tolylfluanid, triadimefon, triadimenol, triazbutil, triazoxide, trichlamide, tricyclazole, tridemorph, triflumizole, triforine, triticonazole, uniconazole, validamycin A, vinclozolin, viniconazole, zarilamide, zineb, ziram and also Dagger G, OK-8705, OK-8801, α-(1,1-dimethylethyl)-β-(2-phenoxyethyl)-1H-1,2,4-triazole-1-ethanol, α-(2,4-dichlorophenyl)-β-fluoro-b-propyl-1H-1,2,4-triazole-1-ethanol, α-(2,4-dichlorophenyl)-β-methoxy-a-methyl-1H-1,2,4-triazole-1-ethanol, α-(5-methyl-1,3-dioxan-5-yl)-β-[[4-(trifluoromethyl)-phenyl]-methylene]-1H-1,2,4-triazole-1-ethanol, (5RS,6RS)-6-hydroxy-2,2,7,7-tetramethyl-5-(1H-1,2,4-triazol-1-yl)-3-octanone, (E)-a-(methoxyimino)-N-methyl-2-phenoxy-phenylacetamide, isopropyl 1-{2-methyl-1-[[[1-(4-methylphenyl)-ethyl]-amino]-carbonyl]-propyl}-carbamate, 1-(2,4-dichlorophenyl)-2-(1H-1,2,4-triazol-1-yl)-ethanone O-(phenylmethyl) oxime, 1-(2-methyl-1-naphthalenyl)-1H-pyrrol-2,5-dione, 1-(3,5-dichlorophenyl)-3-(2-propenyl)-2,5-pyrrolidinedione, 1-[(diiodomethyl)-sulphonyl]-4-methyl-benzene, 1-[[2-(2,4-dichlorophenyl)-1,3-dioxolan-2-yl]-methyl]-1H-

imidazole, 1-[[2-(4-chlorophenyl)-3-phenyloxiranyl]-methyl]-1H-1,2,4-triazole, 1-[1-[2-[(2,4-dichlorophenyl)-methoxy]-phenyl]-ethenyl]-1H-imidazole, 1-methyl-5-nonyl-2-(phenylmethyl)-3-pyrrolidinole, 2',6'-dibromo-2-methyl-4'-trifluoromethoxy-4'-trifluoro-methyl-1,3-thiazole-5-carboxanilide, 2,2-dichloro-N-[1-(4-chlorophenyl)-ethyl]-1-ethyl-3-methyl-cyclopropanecarboxamide, 2,6-dichloro-5-(methylthio)-4-pyrimidinyl thiocyanate, 2,6-dichloro-N-(4-trifluoromethylbenzyl)-benzamide, 2,6-dichloro-N-[[4-(trifluoromethyl)-phenyl]-methyl]-benzamide, 2-(2,3,3-triiodo-2-propenyl)-2H-tetrazole, 2-[(1-methylethyl)-sulphonyl]-5-(trichloromethyl)-1,3,4-thiadiazole, 2-[[6-deoxy-4-O-(4-O-methyl-β-D-glycopyranosyl)-a-D-glucopyranosyl]-amino]-4-methoxy-1H-pyrrolo[2,3-d]pyrimidine-5-carbonitrile, 2-aminobutane, 2-bromo-2-(bromomethyl)-pentanedinitrile, 2-chloro-N-(2,3-dihydro-1,1,3-trimethyl-1H-inden-4-yl)-3-pyridinecarboxamide, 2-chloro-N-(2,6-dimethylphenyl)-N-(isothiocyanatomethyl)-acetamide, 2-phenylphenol (OPP), 3,4-dichloro-1-[4-(difluoromethoxy)-phenyl]-1H-pyrrol-2,5-dione, 3,5-dichloro-N-[cyano-[(1-methyl-2-propynyl)-oxy]-methyl]-benzamide, 3-(1,1-dimethylpropyl-1-oxo-1H-indene-2-carbonitrile, 3-[2-(4-chlorophenyl)-5-ethoxy-3-isoxazolidinyl]-pyridine, 4-chloro-2-cyano-N,N-dimethyl-5-(4-methylphenyl)-1H-imidazole-1-sulphonamide, 4-methyl-tetrazolo[1,5-a]quinazolin-5(4H)-one, 8-(1,1-dimethylethyl)-N-ethyl-N-propyl-1,4-dioxaspiro[4.5]decane-2-methanamine, 8-hydroxyquinoline sulphate, 9H-xanthene-2-[(phenylamino)-carbonyl]-9-carboxylic hydrazide, bis-(1-methylethyl) 3-methyl-4-[(3-methylbenzoyl)-oxy]-2,5-thiophenedicarboxylate, cis-1-(4-chlorophenyl)-2-(1H-1,2,4-triazol-1-yl)-cycloheptanol, cis-4-[3-[4-(1,1-dimethylpropyl)-phenyl-2-methylpropyl]-2,6-dimethyl-morpholine hydrochloride, ethyl [(4-chlorophenyl)-azo]-cyanoacetate, potassium hydrogen carbonate, methanetetrathiol sodium salt, methyl 1-(2,3-dihydro-2,2-dimethyl-1H-inden-1-yl)-1H-imidazole-5-carboxylate, methyl N-(2,6-dimethylphenyl)-N-(5-isoxazolylcarbonyl)-DL-alaninate, methyl N-(chloroacetyl)-N-(2,6-dimethylphenyl)-DL-alaninate, N-(2,3-dichloro-4-hydroxyphenyl)-1-methyl-cyclohexanecarboxamide, N-(2,6-dimethylphenyl)-2-methoxy-N-(tetrahydro-2-oxo-3-furanyl)-acetamide, N-(2,6-dimethylphenyl)-2-methoxy-N-(tetrahydro-2-oxo-3-thienyl)-acetamide, N-(2-chloro-4-nitrophenyl)-4-methyl-3-nitro-benzenesulphonamide, N-(4-cyclohexylphenyl)-1,4,5,6-tetrahydro-2-pyrimidineamine, N-(4-

hexylphenyl)-1,4,5,6-tetrahydro-2-pyrimidineamine, N-(5-chloro-2-methylphenyl)-2-methoxy-N-(2-oxo-3-oxazolidinyl)-acetamide, N-(6-methoxy)-3-pyridinyl)-cyclopropanecarboxamide, N-[2,2,2-trichloro-1-[(chloroacetyl)-amino]-ethyl]-benzamide, N-[3-chloro-4,5-bis(2-propinyloxy)-phenyl]-N'-methoxy-methanimidamide, N-formyl-N-hydroxy-DL-alanine-sodium salt, O,O-diethyl [2-(dipropylamino)-2-oxoethyl]-ethylphosphoramidothioate, O-methyl S-phenyl phenylpropylphosphoramidothioate, S-methyl 1,2,3-benzothiadiazole-7-carbothioate, and spiro[2H]-1-benzopyran-2,1'(3'H)-isobenzofuran]-3'-one.

Bactericides

bronopol, dichlorophen, nitrapyrin, nickel dimethyldithiocarbamate, kasugamycin, octhilinone, furancarboxylic acid, oxytetracyclin, probenazole, streptomycin, tecloftalam, copper sulphate and other copper preparations.

Insecticides / acaricide / nematicides

abamectin, acephate, acetamiprid, acrinathrin, alanycarb, aldicarb, aldoxycarb, alpha-cypermethrin, alphamethrin, amitraz, avermectin, AZ 60541, azadirachtin, azamethiphos, azinphos A, azinphos M, azocyclotin, Bacillus popilliae, Bacillus sphaericus, Bacillus subtilis, Bacillus thuringiensis, baculoviruses, Beauveria bassiana, Beauveria tenella, bendiocarb, benfuracarb, bensultap, benzoximate, betacyfluthrin, bifenazate, bifenthrin, bioethanomethrin, biopermethrin, BPMC, bromophos A, bufencarb, buprofezin, butathiofos, butocarboxim, butylpyridaben, cadusafos, carbaryl, carbofuran, carbophenothion, carbosulfan, cartap, chloethocarb, chlorethoxyfos, chlorfenapyr, chlorfenvinphos, chlorfluazuron, chlormephos, chlorpyrifos, chlorpyrifos M, chlovaporthrin, cis-resmethrin, cispermethrin, clocythrin, cloethocarb, clofentezine, cyanophos, cycloprene, cycloprothrin, cyfluthrin, cyhalothrin, cyhexatin, cypermethrin, cyromazine, deltamethrin, demeton M, demeton S, demeton-S-methyl, diafenthiuron, diazinon, dichlorvos, diflubenzuron, dimethoat, dimethylvinphos, diofenolan, disulfoton, docusat-sodium, dofenapyn,

eflusilanate, emamectin, empenthrin, endosulfan, Entomopfthora spp., esfenvalerate, ethiofencarb, ethion, ethoprophos, etofenprox, etoxazole, etrimfos, fenamiphos, fenazaquin, fenbutatin oxide, fenitrothion, fenothiocarb, fenoxacrim, fenoxycarb, fenpropathrin, fenpyrad, fenpyrithrin, fenpyroximate, fenvalerate, fipronil, fluazinam, fluazuron, flubrocythrinate, flucycloxuron, flucythrinate, flufenoxuron, flutenzine, fluvalinate, fonophos, fosmethilan, fosthiazate, fubfenprox, furathiocarb, granulosis viruses, halofenozide, HCH, heptenophos, hexaflumuron, hexythiazox, hydroprene, imidacloprid, isazofos, isofenphos, isoxathion, ivermectin, nuclear polyhedrosis viruses, lambda-cyhalothrin, lufenuron, malathion, mecarbam, metaldehyde, methamidophos, Metharhizium anisopliae, Metharhizium flavoviride, methidathion, methiocarb, methomyl, methoxyfenozide, metolcarb, metoxadiazone, mevinphos, milbemectin, monocrotophos, naled, nitenpyram, nithiazine, novaluron, omethoat, oxamyl, oxydemethon M, Paecilomyces fumosoroseus, parathion A, parathion M, permethrin, phenthoat, phorat, phosalone, phosmet, phosphamidon, phoxim, pirimicarb, pirimiphos A, pirimiphos M, profenofos, promecarb, propoxur, prothiofos, prothoat, pymetrozine, pyraclofos, pyresmethrin, pyrethrum, pyridaben, pyridathion, pyrimidifen, pyriproxyfen, quinalphos, ribavirin, salithion, sebufos, silafluofen, spinosad, sulfotep, sulprofos, tau-fluvalinate, tebufenozide, tebufenpyrad, tebupirimiphos, teflubenzuron, tefluthrin, temephos, temivinphos, terbufos, tetrachlorvinphos, theta-cypermethrin, thiamethoxam, thiapronil, thiatriphos, thiocyclam hydrogen oxalate, thiodicarb, thiofanox, thuringiensin, tralocythrin, tralomethrin, triarathene, triazamate, triazophos, triazuron, trichlophenidine, trichlorfon, triflumuron, trimethacarb, vamidothion, vaniliprole, Verticillium lecanii, YI 5302, zeta-cypermethrin, zolaprofos, (1R-cis)-[5-(phenylmethyl)-3-furanyl]-methyl 3-[(dihydro-2-oxo-3(2H)-furanylidene)-methyl]-2,2-dimethylcyclopropanecarboxylate, (3-phenoxyphenyl)-methyl 2,2,3,3-tetramethylcyclopropanecarboxylate, 1-[(2-chloro-5-thiazolyl)methyl]tetrahydro-3,5-dimethyl-N-nitro-1,3,5-triazine-2(1H)-imine, 2-(2-chloro-6-fluorophenyl)-4-[4-(1,1-dimethylethyl)phenyl]-4,5-dihydro-oxazole, 2-(acetlyoxy)-3-dodecyl-1,4-naphthalenedione, 2-chloro-N-[[[4-(1-phenylethoxy)-phenyl]-amino]-carbonyl]-benzamide, 2-chloro-N-[[[4-(2,2-dichloro-1,1-difluoro-ethoxy)-phenyl]-amino]-carbonyl]-benzamide, 3-methylphenyl propylcarbamate, 4-

[4-(4-ethoxyphenyl)-4-methylpentyl]-1-fluoro-2-phenoxy-benzene, 4-chloro-2-(1,1-dimethylethyl)-5-[[2-(2,6-dimethyl-4-phenoxyphenoxy)ethyl]thio]-3(2H)-pyridazinone, 4-chloro-2-(2-chloro-2-methylpropyl)-5-[(6-iodo-3-pyridinyl)methoxy]-3(2H)-pyridazinone, 4-chloro-5-[(6-chloro-3-pyridinyl)methoxy]-2-(3,4-dichlorophenyl)-3(2H)-pyridazinone, Bacillus thuringiensis strain EG-2348, [2-benzoyl-1-(1,1-dimethylethyl)-hydrazinobenzoic acid, 2,2-dimethyl-3-(2,4-dichlorophenyl)-2-oxo-1-oxaspiro[4.5]dec-3-en-4-yl butanoate, [3-[(6-chloro-3-pyridinyl)methyl]-2-thiazolidinylidene]-cyanamide, dihydro-2-(nitromethylene)-2H-1,3-thiazine-3(4H)-carboxaldehyde, ethyl [2-[[1,6-dihydro-6-oxo-1-(phenylmethyl)-4-pyridazinyl]oxy]ethyl]-carbamate, N-(3,4,4-trifluoro-1-oxo-3-butenyl)-glycine, N-(4-chlorophenyl)-3-[4-(difluoromethoxy)phenyl]-4,5-dihydro-4-phenyl-1H-pyrazole-1-carboxamide, N-[(2-chloro-5-thiazolyl)methyl]-N'-methyl-N''-nitro-guanidine, N-methyl-N'-(1-methyl-2-propenyl)-1,2-hydrazinedicarbothioamide, N-methyl-N'-2-propenyl-1,2-hydrazinedicarbothioamide, O,O-diethyl [2-(dipropylamino)-2-oxoethyl]-ethylphosphoroamidothioate.

A mixture with other known active compounds, such as herbicides, or with fertilizers and growth regulators is also possible.

The active compounds can be converted into the customary formulations, such as solutions, emulsions, wettable powders, water dispersible granules, suspensions, powders, dusting agents, foaming agents, pastes, soluble powders, granules, suspo-emulsion concentrates, microcapsules, fumigants, natural and synthetic materials impregnated with active compound and very fine capsules and polymeric substances.

These formulations can be prepared according to per se known methods, for example, by mixing the active compounds with extenders, namely liquid, liquefied gas or solid diluents or carriers, and optionally with surface-active agents, namely emulsifiers and/or dispersants and/or foam-forming agents.

If the extender used is water, it is also possible to use, for example, organic solvents as auxiliary solvents. Suitable liquid solvents are essentially: aromatics, such as xylene, toluene, or alkylnaphthalenes, chlorinated aromatics and chlorinated aliphatic hydrocarbons, such as chlorobenzene, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example mineral oil fractions, mineral or vegetable oil, alcohols, such as butanol or glycol, and also their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents, such as dimethylformamide and dimethyl sulphoxide, and also water.

Liquefied gas diluents or carriers are liquefied substances which are gases at normal temperature and pressure. Liquefied gas diluents can be, for example, aerosol propellants such as butane, propane, nitrogen gas, carbon dioxide, halogenated hydrocarbons, etc.

Suitable solid carriers are, for example, ammonium salts and ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, ground synthetic minerals, such as finely divided silica, alumina and silicates; suitable solid carriers for granules are, for example, crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, as well as synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks; suitable emulsifiers and/or foam-formers are, for example, nonionic and anionic emulsifiers, such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers such as alkylaryl polyglycol ethers, alkylsulphonates, alkyl sulphates, arylsulphonates and protein hydrolysates; suitable dispersants are, for example, lignin-sulphite waste liquors and methylcellulose.

Suitable tackifiers are, for example, carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, as well as natural phospholipids, such as cephalins and

lecithins, and synthetic phospholipids, can be used in the formulations. Other additives can be mineral and vegetable oils.

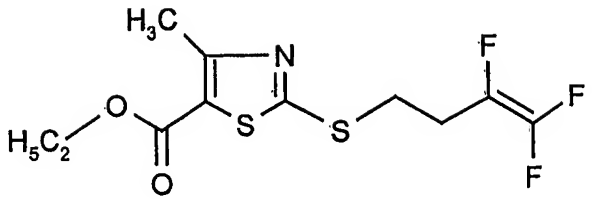
It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs and metal phthalocyanine dyestuffs, and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

Said formulations can contain in a range of generally 0.1-95 % by weight, preferably 0.5-90 % by weight of the aforementioned active components.

Then the preparations and applications of the compounds of the present invention will be described more specifically by the following examples. However, the present invention should not be restricted to them in any way. "Parts" mean "parts by weight" unless specified.

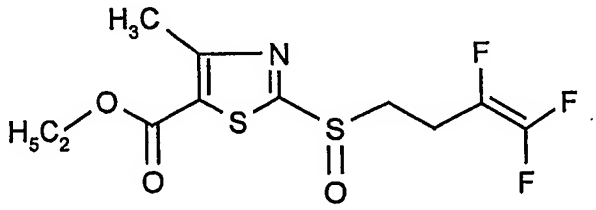
EXAMPLES

Synthesis Example 1



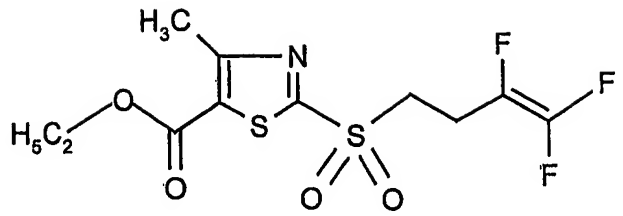
0.98 g (4.82 mmol) of 5-ethoxycarbonyl-2-mercapto-4-methylthiazole, 0.8 g (5.79 mmol) of potassium carbonate and 0.91g (4.82mmol) of 4-bromo-1,1,2-trifluoro-1-butene were suspended in 30ml of acetonitrile and refluxed for 4 hours. The deposited precipitates were filtered and the filtrate was concentrated under reduced pressure. The residue was subjected to column chromatography (hexane:ethyl acetate = 9:1) to obtain 0.97g of 5-ethoxycarbonyl-4-methyl-2-(3',4',4'-trifluoro-3'-butenylthio)thiazole. mp 40-43°C. Yield: 65%.

Synthesis Example 2



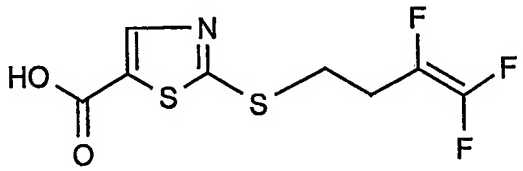
0.93 g (2.99 mmol) of 5-ethoxycarbonyl-4-methyl-2-(3',4',4'-trifluoro-3'-butenylthio)-thiazole was dissolved in 30ml of dichloromethane and 0.72 g (4.18 mmol) of m-chloroperbenzoic acid (purity about 70%) was added little by little. After stirring at room temperature for 8 hours the reaction mixture was washed with saturated sodium hydrogen carbonate and water, and dried over anhydrous sodium sulfate. The solvent was distilled off under reduced pressure and the residue was subjected to column chromatography (hexane:ethyl acetate = 3:1) to obtain 0.77g of 5-ethoxycarbonyl-4-methyl-2-(3',4',4'-trifluoro-3'-butenylsulfinyl)thiazole. $n_D^{20} = 1.5145$. Yield: 79%.

Synthesis Example 3



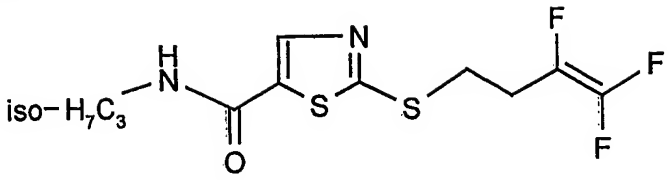
0.86 g (2.76 mmol) of 5-ethoxycarbonyl-4-methyl-2-(3',4',4'-trifluoro-3'-butenylthio)-thiazole was dissolved in 30ml of dichloromethane and 1.33 g (7.73 mmol) of m-chloroperbenzoic acid (purity about 70%) was added little by little. After stirring at room temperature for 8 hours the reaction mixture was washed with saturated sodium hydrogen carbonate and water, and dried over anhydrous sodium sulfate. The solvent was distilled off under reduced pressure and the residue was subjected to column chromatography (hexane:ethyl acetate = 4:1) to obtain 0.81g of 5-ethoxycarbonyl-4-methyl-2-(3',4',4'-trifluoro-3'-butenylsulfonyl)thiazole. n_D^{20} = 1.4960. Yield: 85%.

Synthesis Example 4



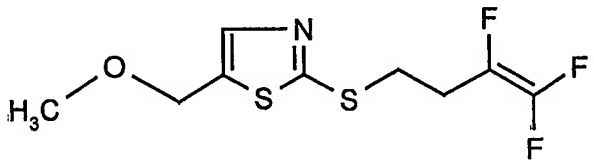
13.5 g (60 mmol) of 2-(3',4',4'-trifluoro-3'-butenylthio)thiazole was dissolved in 250 ml of absolute ether and 41.3ml of n-butyllithium (1.6 M hexane solution) was slowly added dropwise at -75°C. After addition the mixture was stirred at -75°C for 1 hour, to which an excess amount of dry ice was added and the temperature was brought back to room temperature under stirring overnight. Then the reaction mixture was diluted with water, acidified with 1N hydrochloric acid and extracted with ethyl acetate. The extract was washed with water and dried over anhydrous magnesium sulfate. The solvent was distilled off under reduced pressure to obtain 15g of 5-carboxy-2-(3',4',4'-trifluoro-3'-butenylthio)thiazole. mp 93-96°C. Yield: 93%.

Synthesis Example 5



3.2 g (11.88mmol) of 5-carboxy-2-(3',4',4'-trifluoro-3'-butenylthio)thiazole was dissolved in 50ml of chloroform, to which 1.7 g (14.29mmol) of thionyl chloride and a drop of dimethylformamide were added and heated at 50°C for 4 hours. After cooling, the solvent was distilled off under reduced pressure and 15 ml of dichloromethane was added to the residue to obtain a solution of an acid chloride. To the solution a dichloromethane (15 ml) solution of 1.76 g (29.78 mmol) of isopropylamine was added dropwise. After stirring at room temperature for 4 hours, the mixture was washed with 1N hydrochloric acid and water, and dried over anhydrous sodium sulfate. After the solvent was distilled off under reduced pressure, the residue was subjected to column chromatography (hexane:ethyl acetate = 4:1) to obtain 2.8 g of 5-isopropylaminocarbonyl-2-(3',4',4'-trifluoro-3'-butenylsulfonyl)-thiazole. mp 133-134°C. Yield: 76%.

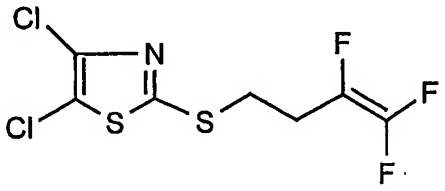
Synthesis Example 6



8.8 g (39.07 mmol) of 2-(3',4',4'-trifluoro-3'-butenylthio)thiazole was dissolved in 40 ml of absolute ether and 26.8ml of n-butyllithium (1.6 M hexane solution) was slowly added dropwise at -75°C. After addition the mixture was stirred at -75°C for 1 hour, to which an anhydrous ether solution (20 ml) of 5.37g (42.97 mmol) of bromomethyl methyl ether was added dropwise during 15 minutes. After addition, the mixture was stirred at room temperature for 1 hour, to which 30 g of ice and

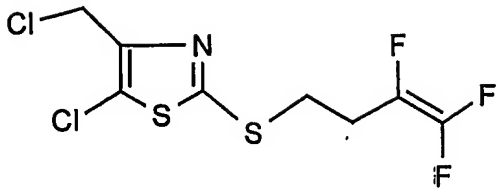
water were added to stop the reaction. The organic layer and the water layer were separated. The water layer was extracted with ether and the extract was combined with the organic layer. After washing with saturated aqueous solution of sodium chloride, the organic layer was dried over anhydrous magnesium sulfate. After the solvent was distilled off under reduced pressure, the residue was subjected to column chromatography (hexane:ethyl acetate = 4:1) to obtain 6g of 5-methoxymethyl-2-(3',4',4'-trifluoro-3'-butenylsulfonyl)thiazole. $n_D^{20} = 1.5157$. Yield: 57%.

Synthesis Example 7



4.25 g (22.57 mmol) of 2,4,5-trichlorothiazole and 1.72 g (22.57 mmol) of thiourea were dissolved in 50 ml of ethanol and refluxed for 8 hours. After cooling, the solvent was distilled off under reduced pressure and the residue was dissolved in 50 ml of acetone. To the solution 4.48 g (23.7 mmol) of 4-bromo-1,1,2-trifluoro-1-butene and 3.28 g (23.7 mmol) of potassium carbonate werre added and refluxed for 5 hours. After filtering off the deposited precipitates, the filtrate was concentrated under reduced pressure and the residue was purified by column chromatography (hexane:ethyl acetate = 19:1) to obtain 0.45 g of 4,5-dichloro-2-(3',4',4'-trifluoro-3'-butenylthio)thiazole. Yield: 7% (oily substance).

Synthesis Example 8

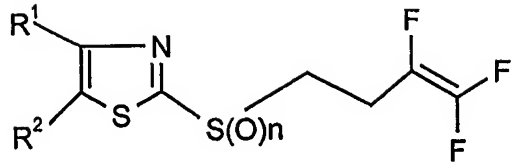


1.55 g (6.48 mmol) of 4-methyl-2-(3',4',4'-trifluoro-3'-butenylthio)thiazole was dissolved in 40 ml of carbon tetrachloride, to which 1.73 g (12.96 mmol) of N-chlorosuccinimide was added and refluxed for 2 hours by heating. After cooling, the deposited precipitates were filtered off and the solvent was distilled off under reduced pressure. The residue was purified by column chromatography (hexane:ethyl acetate = 19:1) to obtain 1.8 g of 5-chloro-4-chloromethyl-2-(3',4',4'-trifluoro-3'-butenylthio)thiazole. n_D^{20} = 1.5269. Yield: 90%.

The following compounds of the formula (I) (Table I) of the present invention can be synthesized by the same process as shown in Synthesis Examples 1-8.

The compounds obtained in Synthesis Examples 1-8 are also shown in Table 1.

Table 1



(I)

Compound No.	R^1	R^2	n	mp or n_D^{20}
1	H	$-CH_3$	0	
2	H	$-C_2H_5$	0	
3	H	$-CH_2O-CH_3$	0	1.5157
4	H	$-CH_2O-CH_3$	1	
5	H	$-CH_2O-CH_3$	2	1.5012
6	H	$-CH_2O-C_2H_5$	0	
7	H	$-CH_2O-C_2H_5$	2	
8	H	$-CH_2S-CH_3$	0	1.5120
9	H	$-CH_2S-C_2H_3$	0	
10	H	-C(O)OH	0	93-96
11	H	$-C(O)NH-CH_3$	0	100-101
12	H	$-C(O)NH-CH_3$	1	
13	H	$-C(O)NH-CH_3$	2	1.4990
14	H	$-C(O)NH-C_2H_5$	0	
15	H	$-C(O)NH-n-C_3H_7$	0	
16	H	$-C(O)NH-i-C_3H_7$	0	133-134
17	H	$-C(O)NH-i-C_3H_7$	2	105-107
18	H	-C(O)NH 	0	106-108
19	H	-C(O)NH 	0	
20	H	-C(O)NH 	0	
21	H	$-C(O)NH-n-C_4H_9$	0	

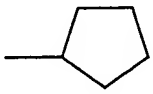
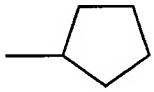
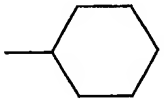
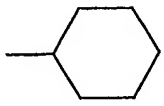
Table 1 (continued)

Compound No.	R^1	R^2	n	mp or n_D^{20}
22	H	-C(O)NH-sec-C_4H_9	0	100-102
23	H	-C(O)N$(CH_3)_2$	0	1.5488
24	H	-C(O)N$(CH_3)_2$	1	
25	H	-C(O)N$(C_2H_5)_2$	0	1.5414
26	H	-C(O)N$(C_2H_5)_2$	2	
27	F	H	0	
28	Cl	H	0	oil
29	Cl	H	1	
30	Cl	H	2	oil
31	Cl	Cl	0	oil
32	Cl	Cl	1	
33	Cl	Cl	2	oil
34	Br	H	0	
35	Br	H	1	
36	-CH_3	H	1	1.5140
37	-CH_3	H	2	1.4965
38	-CH_3	Cl	0	1.5273
39	-CH_3	Cl	1	
40	-CH_3	Cl	2	1.5165
41	-CH_3	-CH_3	0	1.5041
42	-CH_3	-CH_3	1	
43	-CH_3	-CH_3	2	
44	-CH_3	-C(O)OCH_3	0	1.5280
45	-CH_3	-C(O)OCH_3	1	1.5200
46	-CH_3	-C(O)OCH_3	2	1.6225
47	-CH_3	-C(O)OC_2H_5	0	40-43

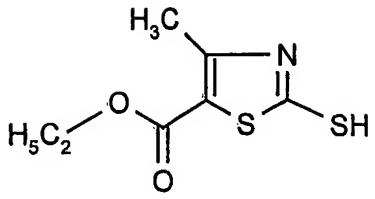
Table 1 (continued)

Compound No.	R^1	R^2	n	mp or n_D^{20}
48	$-CH_3$	$-C(O)OC_2H_5$	1	1.5145
49	$-CH_3$	$-C(O)OC_2H_5$	2	1.4960
50	$-CH_3$	$-C(O)O\text{-}n\text{-}C_3H_7$	0	
51	$-CH_3$	$-C(O)O\text{-}i\text{-}C_3H_7$	0	
52	$-C_2H_5$	H	0	1.5072
53	$-C_2H_5$	H	1	1.5115
54	$-C_2H_5$	H	2	1.4955
55	$-C_2H_5$	$-CH_3$	0	
56	$-n\text{-}C_3H_7$	H	0	
57	$-n\text{-}C_3H_7$	H	1	
58	$-n\text{-}C_3H_7$	H	2	
59	$-i\text{-}C_3H_7$	H	0	1.4973
60	$-i\text{-}C_3H_7$	H	1	1.5041
61	$-i\text{-}C_3H_7$	H	2	1.4889
62	$n\text{-}C_4H_9$	H	0	
63	$n\text{-}C_4H_9$	H	1	
64	$t\text{-}C_4H_9$	H	0	1.4965
65	$t\text{-}C_4H_9$	H	2	
66	$ClCH_2$	H	0	
67	$ClCH_2$	Cl	0	1.5269
68	$BrCH_2$	H	0	
69	CF_3	H	0	1.4635
70	CF_3	H	1	1.4710

Table 1 (continued)

Compound No.	R^1	R^2	n	mp or n_D^{20}
71	CF_3	H	2	48-51
72		H	0	1.5254
73		H	1	1.4955
74		H	2	1.5148
75		H	0	
76		H	1	
77		H	0	
78		H	1	
79	$-CH_2-C(O)OCH_3$	H	0	
80	$-CH_2-C(O)OCH_3$	H	1	
81	$-CH_2-C(O)-OC_2H_5$	H	0	1.5040
82	$-CH_2-C(O)-OC_2H_5$	H	1	1.5064
83	$-CH_2-C(O)-OC_2H_5$	H	2	1.4945
84	$-CH_2-C(O)-O-n-C_3H_7$	H	0	
85	$-CH_2-C(O)-O-n-C_3H_7$	H	2	

Synthesis Reference Example



1.65 g (10 mmol) of ethyl 2-chloroacetoacetate and 1.1g (10 mmol) of ammonium dithiocarbamate were suspended in 30ml of ethanol and refluxed for 4 hours. After cooling, the deposited precipitates were filtered and the filtrate was concentrated under reduced pressure. After adding water, the residue was extracted with ethyl acetate. The extract was washed with water and dried with anhydrous sodium sulfate. The solvent was distilled off under reduced pressure and the residue was subjected to column chromatography (hexane:ethyl acetate = 2:1) to obtain 1.1g of 5-ethoxycarbonyl-2-mercapto-4-methylthiazole. mp 136-137°C. Yield: 54%.

TEST EXAMPLES

Test Example 1

Test for *Meloidogyne spp.* (Soil pot test)

Preparation of test agent

1 Part of the active compound is impregnated to 99 parts of pumice to obtain fine granules.

Test method

The test agent prepared as mentioned above was added to soil contaminated with *Meloidogyne incognita* to a chemical concentration of 10 ppm and homogeneously mixed by stirring. A pot (1/5000 are) was filled with the soil. About 20 seeds of tomato (variety: Kurihara) were sown per pot. After cultivation in a greenhouse for 4 weeks, they were carefully pulled out not to damage the roots and the root knot index and the controlling effect were determined as follows.

Degree of damage	0:	No knots were formed (Complete control)
	1:	A few knots were formed.
	2:	Knots were formed to a medium extent.
	3:	Knots were formed to an intense extent.
	4:	Knots were formed to the most intense extent (which corresponds to non-treatment).

$$\text{Root knot index} = \frac{\Sigma\,(\text{degree of damage} \times \text{number of individuals})}{\text{Total number of tested individuals} \times 4} \times 100$$

The controlling effect of the compounds tested can then be evaluated according to the following equation:

$$\text{Controlling effect [\%]} = \frac{(\text{Root knot index at non-treated area} - \text{Root knot index at treated area})}{\text{Root knot index at non-treated area}} \times 100$$

In the test described, the following compounds show more than 90 % controlling effect at an effective concentration of 10 ppm: Compounds No. 25, 36, 38, 52, 53, 72 and 73.

Formulation Examples

Formulation Example 1 (Granule)

To a mixture of 10 parts of the compound of the present invention (No. 25), 30 parts of bentonite (montmorillonite), 58 parts of talc and 2 parts of ligninsulphonate salt, 25 parts of water are added, well kneaded, made in granules of 10-40 mesh by extrusion granulator and dried at 40-50°C to obtain granules.

Formulation Example 2 (Granule)

95 Parts of clay mineral particles having a particle diameter distribution of 0.2-2 mm are put into a rotary mixer. While rotating it, 5 parts of the compound of the present invention (No. 36) are sprayed together with a liquid diluent, wetted uniformly and dried at 40-50°C to obtain granules.

Formulation Example 3 (Emulsifiable concentrate)

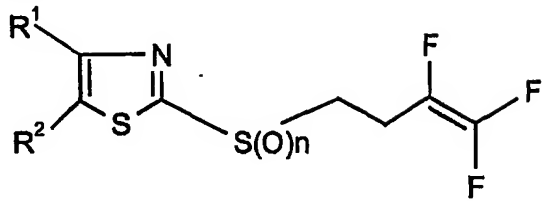
30 Parts of the respective compound of the present invention (No. 52), 55 parts of xylene, 8 parts of polyoxyethylene alkyl phenyl ether and 7 parts of calcium alkylbenzenesulphonate are mixed and stirred to obtain an emulsifiable concentrate.

Formulation Example 4 (Wettable powder)

15 Parts of the respective compound of the present invention (No. 72), 80 parts of a mixture of white carbon (hydrous amorphous silicon oxide fine powders) and powder clay (1:5), 2 parts of sodium alkylbenzenesulphonate and 3 parts of sodium alkylnaphthalenesulphonate-formalin-condensate are crushed and mixed to produce a wettable powder.

Claims:

1. A compound of the formula (I)



(I),

wherein

R^1 represents hydrogen, halogen, alkyl, haloalkyl, cycloalkyl or alkoxycarbonylmethyl,

R^2 represents hydrogen, halogen, alkyl, alkoxyalkyl, alkylthioalkyl, carboxy, alkylaminocarbonyl, cycloalkylaminocarbonyl, dialkylaminocarbonyl or alkoxycarbonyl, and

n represents 0, 1 or 2,

with the proviso that R^1 and R^2 do not represent hydrogen at the same time, and in case R^1 represents hydrogen, then R^2 does not represent halogen.

2. A compound of the formula (I) according to claim 1, wherein

R^1 represents hydrogen, fluoro, chloro, bromo, C_{1-6}-alkyl or C_{1-3}-haloalkyl, C_{3-6}-cycloalkyl or C_{1-4}-alkoxycarbonylmethyl,

R^2 represents hydrogen, fluoro, chloro, bromo, carboxy, C_{1-6}-alkyl, C_{1-4}-alkoxy-C_{1-4}-alkyl, C_{1-4}-alkylthio-C_{1-4}-alkyl, C_{1-4}-alkylaminocarbonyl, C_{3-6} cycloalkylaminocarbonyl, di-C_{1-4}-alkylaminocarbonyl or C_{1-4}-alkoxycarbonyl, and

n represents 0 or 2.

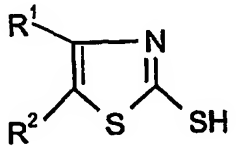
3. A compound of the formula (I) according to claim 1 or claim 2, wherein

R^1 represents hydrogen, fluoro, chloro, bromo, methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, chloromethyl, bromomethyl, trifluoromethyl, cyclopropyl, cyclopentyl, cyclohexyl, methoxycarbonylmethyl, ethoxycarbonylmethyl or n-propoxycarbonylmethyl,

R^2 represents hydrogen, chloro, methyl, ethyl, methoxymethyl, ethoxymethyl, methylthiomethyl, ethylthiomethyl, carboxy, methylaminocarbonyl, ethylaminocarbonyl, n-propylaminocarbonyl, isopropylaminocarbonyl, n-butylaminocarbonyl, sec-butylaminocarbonyl, cyclopropylaminocarbonyl, cyclopentylaminocarbonyl, cyclohexylaminocarbonyl, dimethylaminocarbonyl, diethylaminocarbonyl, methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl or isopropoxycarbonyl, and

n represents 0.

4. A process for preparing a compound of the formula (I) according to claim 1, characterized, in case n represents 0, in that compounds of the formula (II)

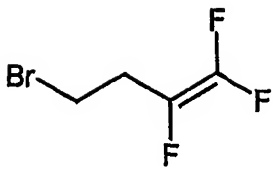


(II)

wherein

R^1 and R^2 have the aforementioned definitions,

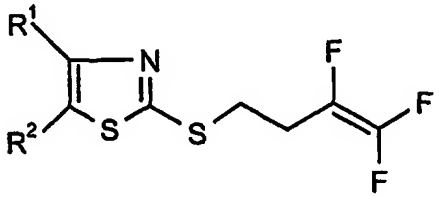
are reacted with 4-bromo-1,1,2-trifluoro-1-butene



in the presence of inert solvents and, if appropriate, in the presence of an acid binder ("preparation process (a)"),

or, in case n represents 1 or 2,

in that compounds of the formula (Ia)



(Ia)

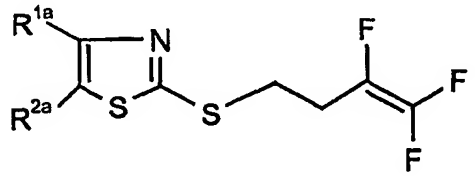
wherein

R^1 and R^2 have the aforementioned definitions,

are oxidized in the presence of inert solvents ("preparation process (b)"),

or, in case R^1 represents haloalkyl, R^2 represents hydrogen and n represents 0,

in that compounds of the formula (Ib)



(Ib)

wherein

R^{1a} represents alkyl, and

R^{2a} represents hydrogen,

are reacted with a halogenating agent in the presence of inert solvents ("preparation process (c)").

5. Nematicidal compositions, characterized in that they contain at least one compound of the formula (I) according to claims 1 to 4 and customary extenders.

6. A method of combating nematodes, characterized in that compounds of the formula (I) according to claims 1 to 4 are allowed to act on nematodes and/or their habitat.

7. Use of the compounds of formula (I) according to claims 1 to 4 for combating nematodes.

8. Process for preparing nematicidal compositions, characterized in that the compounds of the formula (I) according to claims 1 to 4 are mixed with extenders and/or surface active agents.

INTERNATIONAL SEARCH REPORT

Internal Application No
PCT/EP 02/10351

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07D277/36 A01N43/78

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ, WPI Data, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 01 02378 A (BAYER AGROCHEM KK ;SHIBUYA KATSUHIKO (JP); OTSU YUICHI (JP); ABE T) 11 January 2001 (2001-01-11) claims; examples 1-3	1-9
Y	WO 86 07590 A (FMC CORP) 31 December 1986 (1986-12-31) claims; example 16	1-9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 November 2002	25/11/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Menegaki, F

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 02/10351

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [X] Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

Although claims 7,8 are directed, i.a., to a method of treatment of the human/animal body, since human/animal body is not excluded as a host, the search has been carried out and based on the alleged effects of the compound/composition.

2. [ ] Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. [ ] As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest.

[ ] No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 02/10351

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0102378 A	11-01-2001	JP 2001019685 A	23-01-2001
		AU 5242000 A	22-01-2001
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		WO 0102378 A1	11-01-2001
		TR 200200068 T2	21-05-2002
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		MX 9249 A	01-12-1993
		US 4952580 A	28-08-1990